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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Stabilised PVC Compositions for the Preparation of Mouldings

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(57) 7 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.

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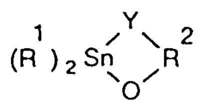
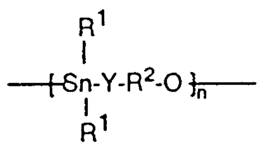
Abstract of the Disclosure

There is described the use of

(a) at least one organotin compound of formula I or II



(I),

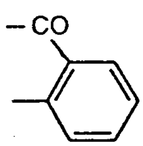


(II),

wherein n is a number from 1 to 6,

R^1 is C_4-C_8alkyl,

Y is -S- or -O- ,

if Y is -S-, then R^2 is $-(CH_2)_2$-CO- or  ,

if Y is -O- , then R^2 is -CO-R^3-CO- , and

R^3 is C_1-C_{12}alkylene, C_2-C_{12}alkenylene or o- or p-phenylene, as well as of

(b) at least one perchlorate of a mono- or divalent metal

in polymer compositions comprising

(c) 20-80 parts by weight of a vinyl chloride homopolymer (PVC),

(d) 80-20 parts by weight of at least one thermoplastic copolymer based on styrene and acrylonitrile.

These compositions have enhanced resistance to thermal and mechanical stress and can be processed well by the injection moulding or extrusion process to mouldings having superior thermostability.

Stabilised PVC compositions for the preparation of mouldings

The invention relates to the use of compositions consisting of a vinyl halide homopolymer (PVC) and a thermoplastic copolymer based on styrene and acrylonitrile, comprising at least one organotin compound and one perchlorate of a mono- or divalent metal as stabiliser combination, in processes for the preparation of mouldings.

Organotin compounds are usually employed as stabilisers in the extrusion and injection moulding process of PVC/ABS compounds. In such processes, the material may be stressed twofold: by shear forces (fricative) on the one hand and and by high temperatures on the other hand. In both cases, stress is increased by extended residence times in the processing apparatus.

In the case of PVC/ABS injection moulding compositions a thermostability as high as possible is aimed at because this is advantageous for processing and application. Solid instead of liquid organotin stabilisers are therefore typically used which, however, have the disadvantage of increasing the melt viscosity. This disadvantage can be met in part by processing at elevated temperatures, but this in turn may lead to thermal degradation phenomena (discoloration of the product and impairment of its mechanical properties).

Another disadvantage of the solid organotin stabilisers is that the composition adheres more strongly to the surface areas of the processing machine so that friction and shear forces can damage the material. The addition of lubricants offers only limited compensation for this because these lubricants have a harmful effect on the thermo-stability.

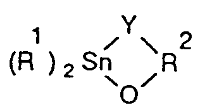
Search continues for effective stabiliser combinations for such applications which offer maximum protection against degradation by thermal and mechanical stress while retaining the thermostability.

Organotin compounds and salts of halogen oxy acid have been used as stabilisers for PVC (JP 78-59,744). The combination of perchlorates and organotin compounds has also been proposed for increasing the thermostability of PVC sheets (EP-A-0-574 348).

It has also been recommended to use specific organotin compounds together with thioethers (or also with disulfides) and perchlorates for stabilising PVC (JP Kokai 01-236 252, JP Kokai 03 168 241).

It has now been found that by using a stabiliser combination of specific organotin compounds and perchlorates containing tin/oxygen bonds it is possible to process PVC/ABS blends and compounds surprisingly unproblematically and without the above disadvantages by the injection moulding or extrusion process to products having superior thermostability.

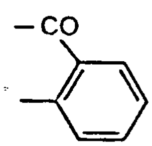
Accordingly, the invention relates to the use of
(a) at least one organotin compound of formula I or II



(I),

$$-\!\!\left[\begin{matrix} R^1 \\ | \\ Sn \\ | \\ R^1 \end{matrix}\!\!-Y-R^2-O\right]_n\!\!- \qquad \text{(II)},$$

wherein n is a number from 1 to 6,
R^1 is C_4-C_8alkyl,
Y is -S- or -O-,

if Y is -S-, then R^2 is $-(CH_2)_2-CO-$ or  ,

if Y is -O-, then R^2 is $-CO-R^3-CO-$, and
R^3 is C_1-C_{12}alkylene, C_2-C_{12}alkenylene or o- or p-phenylene, as well as of
(b) at least one perchlorate of a mono- or divalent metal

for the preparation of stabilised mouldings having superior thermostability and consisting of polymer compositions, comprising
(c) 20-80 parts by weight of a vinyl chloride homopolymer (PVC),
(d) 80-20 parts by weight of at least one thermoplastic copolymer based on styrene and

acrylonitrile

by the injection moulding or extrusion process.

Component (d) may in particular be a copolymer from the ABS and SAN group. In this connection ABS means: acrylonitrile/butadiene/styrene(graft polymer consisting of styrene and acrylonitrile/butadiene rubber) and SAN means: styrene/acrylonitrile copolymer.

The compositions preferably comprise 20 to 50% of component (c) and 80 to 50% of component (d).

It is also preferred to use polymer compositions comprising as components (c) and (d) a mixture of 25-75 % by weight of PVC and 75-25% of the cited copolymers. Illustrative examples of such compositions are: 25-50 % by weight of PVC and 75-50 % by weight of copolymers, or 40-75 % by weight of PVC and 60-25 % by weight of copolymers. Preferred copolymers are ABS and SAN, in particular ABS. The compositions may comprise one copolymer or both copolymers.

"Compositions" will hereinafter be understood to mean compositions which consist of at least the above-described components (a) to (d).

The compositions can contain further copolymers as modifiers. In addition to those cited above, these may also be NBR (acrylonitrile/butadiene), NAR (acrylonitrile/acrylate) or EVA (ethylene/vinyl acetate). It is also possible to use the cited copolymers themselves as modifiers. The use of modifiers, e.g. as blends or as graft copolymers, for improving the performance characteristics is known to the expert. Preferably up to 20 parts by weight of modifiers may be present, based on the sum of (c) and (d).

As is known from the chemistry of organotin stabilisers, the latter are often present in the stabilised substrate in a form other than that in which they were added. Reaction (comproprionation) products are usually formed. The invention naturally also relates to the use of compositions containing such products formed from the compounds of component (c), corresponding to formulae I and II.

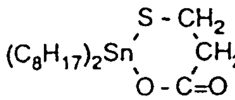
The organotin compounds of formulae I and II are known (see, for example, the references cited at the outset as well as US 5 021 491 and references therein: US 2 731 482, US 2 731 484, US 2 713 585, US 2 648 650, US 3 507 827). The organotin compounds

may in particular be carboxylates or mercaptocarboxylates:

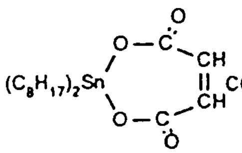
A typical mercaptocarboxylate is polymeric di-n-butyl tin mercaptopropionate, $[(n\text{-}C_4H_9)_2Sn\text{-}S\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}O]_n$.

Typical carboxylates are polymeric di-n-butyl tin maleate or di-n-octyl tin maleate.

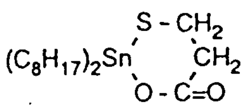
Mixtures may also be used, typically the mixture consisting of 40 % by weight of the



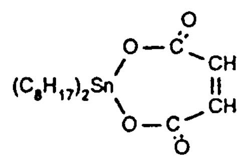
compound and 60 % by weight of the



compound; or the mixture consisting of 66.7 % by weight of the



compound and 33.3 % by weight of the



compound.

Component (a) is preferably present in the compositions in an amount of 0.5 to 5%, based on [(c) + (d)].

In addition to the compounds of component (a) of formulae I and II, further tin stabilisers may also be present in the compositions, provided they do not adversely affect the improved properties achieved by said compounds, However, preference is given to compositions which contain no further tin stabilisers in addition to the above-described organotin compounds of component (a) and the comproportionation products thereof.

R^1 defined as C_4-C_8alkyl is typically n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, hexyl, heptyl, octyl, isooctyl or 2-ethylhexyl,

R^1 is preferably butyl or octyl, in particular n-butyl, n-octyl or isooctyl.

R^3 defined as C_2-C_{12}alkenylene is a divalent alkenyl radical and is typically derived from the following alkenyl radicals: ethenyl, propenyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl. Among these, C_2-C[illegible]alkenylene radicals are preferred.

R^3 defined as C_1-C_{12}alkylene is a divalent alkyl radical within the scope of the indicated chain lengths, typically methylene, ethylene, -$CH(C_1$-C_{10}alkyl)-CH_2- (for example

(a) to 1 part by weight (b).

The compositions are prepared by known processes. The stabilisers are admixed to the polymer blends in known manner before or during processing. A homogeneous mixture can be obtained e.g. before processing by using a heating-cooling mixer usually at 120°C in the heating phase.

The compositions can advantageously also comprise conventional amounts of further, customary PVC stabilisers and/or further additives, typically epoxy compounds, metal soaps, which are mainly metal carboxylates and metal phenolates of metals of the second main and auxiliary group of the periodic table, or also inorganic salts of metals of the second auxiliary group of the periodic table, as well as antioxidants.

The further stabilisers just mentioned are preferably incorporated in amounts of 0.05 to 6 %, more preferably of 0.1 to 3 %, based on the entire composition.

Metal soaps are mainly metal carboxylates, preferably long-chain carboxylic acids. Common examples are stearates and laurates, as well as oleates and salts of short-chain alkylcarboxylic acids. So-called synergistic mixtures are often used, such as barium/zinc, magnesium/zinc, calcium/zinc or calcium/magnesium/zinc stabilisers. The metal soaps can be used singly or in admixture. A survey of customary metal soaps may be found in Ullmanns Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A16 (1985) S.361 ff). Further stabilisers may also be metal carboxylates and metal phenolates of metals of the second main and auxiliary group of the periodic table, or also inorganic salts of metals of the second auxiliary group of the periodic table, typically $ZnCl_2$.

Illustrative examples of metal carboxylates are the metal salts of saturated, unsaturated or hydroxyl group-substituted aliphatic carboxylic acids containing 6 to 20 carbon atoms, typically hexanoic acid, heptanoic acid, octanoic acid, 2-ethylhexanoic acid, undecylanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, 12-oxystearic acid, oleic acid, linoleic acid or ricinoleic acid. Metal salts of aromatic carboxylic acids, such as substituted phenylbenzoates, also merit interest. Preferred metals are those of the series of Ba, Sr, Ca, Mg, Zn and Cd. Preferred metal carboxylates are typically calcium stearate or zinc stearate, barium p-tert-butylbenzoate, zinc oleate and calcium oleate.

Suitable metal phenolates are in particular the metal salts of phenols containing

6-20 carbon atoms, typically alkylphenols, such as p-tert-butylphenol, p-octylphenol, p-nonylphenol or p-dodecylphenol. A typical example thereof is barium p-n-nonylphenolate.

Preferred antioxidants are alkylated monophenols, alkylidene bisphenols and propionates substituted by sterically hindered phenol radicals, e.g. 2,6-di-tert-butyl-p-cresol, 2,2-bis-(4'-hydroxyphenyl)propane and n-octadecyl ß-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

Depending on the end use requirement of the compositions, further additives known to the expert can also be incorporated before or during the incorporation of the stabiliser, typically lubricants (preferably montan waxes or glycerol esters), fatty acid esters, paraffins, plasticisers, fillers, carbon black, kaolin, TiO_2, talcum, silicates, hydrotalcites, zeolites, glass fibres, pigments, light stabilisers, UV absorbers, flame retardants and antistatics.

Among these additives, lubricants, pigments, processing assistants, fillers, antioxidants and/or light stabilisers are preferred.

Suitable compounds of the hydrotalcite or zeolite series are the naturally occuring minerals as well as synthetically produced compounds. It is preferred to use additional hydrotalcites and/or zeolites in the compositions because these compounds can enhance the stabilisation synergistically.

The chemical composition of the hydrotalcites and zeolites is known to the expert.

Compounds of the hydrotalcite series can be represented by the general formula III,

$$M^{2+}{}_{1-x} \cdot M^{3+}{}_{x} \cdot (OH)_2 \cdot (A^{n-})_{x/n} \cdot mH_2O \qquad \text{(III)},$$

wherein

M^{2+} = Mg, Ca, Sr, Zn, Sn and/or Ni,

M^{3+} = Al, B or Bi,

A^n is an anion having the valency n,

n is a number from 1 to 4,

x is a number from 0 to 0.5,

m is a number from 0 to 20.

A^n is preferably OH^-, Cl^-, Br^-, I^-, ClO_4^-, HCO_3^-, CH_3COO^-, $C_6H_5COO^-$, CO_3^{2-}, SO_4^{2-}, $\begin{array}{l}COO^- \\ | \\ COO^-\end{array}$, $(CHOHCOO)_2^{2-}$, $(CHOH)_4CH_2OHCOO^-$. $C_2H_4(COO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $CH_3CHOHCOO^-$, SiO_3^{2-}, SiO_4^{4-}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ or HPO_4^{2-} ; further examples are disclosed in DE 41 06 403.

Other hydrotalcites which can expediently be used are compounds of the general formula IIIa

$$M_x^{2+}Al_2(OH)_{2x+6nz}(A^{n-})_2 \cdot mH_2O \qquad \text{(IIIa)},$$

in which formula IIIa M^{2+} is at least one metal of the series of Mg and Zn, preferably Mg,

A^{n-} is an anion, typically of the series of CO_3^{2-}, $\left(\begin{array}{l}COO \\ | \\ COO\end{array}\right)^{2-}$, OH^- und S^{2-}, wherein n is the valency of the anion, m is a positive number, preferably from 0.5 to 15, and x and z are positive numbers, x preferably being a number from 2 to 6, and z being less than 2.

Illustrative examples of hydrotalcites are:

$Al_2O_3 \cdot 6MgO \cdot CO_2 \cdot 12H_2O$,

$Mg_{4.5}Al_2)_{13} \cdot CO_3 \cdot 3.5H_2O$,

$4MgO \cdot Al_2O_3 \cdot CO_2 \cdot 9H_2O$,

$4MgO \cdot Al_2O_3 \cdot CO_2 \cdot 6H_2O$,

$ZnO \cdot 3MgO \cdot Al_2O_3 \cdot CO_2 \cdot 8\text{-}9H_2O$, or

$ZnO \cdot 3MgO \cdot Al_2O_3 \cdot CO_2 \cdot 5\text{-}6H_2O$.

Zeolites can be represented by the general formula (IV)

$M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$ (IV),

wherein n is the charge of the cation M;
M is an element of the first or second main group of the periodic table, such as Li, Na, K, Mg, Ca, Sr or Ba;
y : x is a number from 0.8 to 15, preferably from 0.8 to 1.2; and
w is a number from 0 to 300, preferably from 0.5 to 30.

Illustrative examples of zeolites are sodium aluminium silicates of formulae

$Na_{12}Al_{12}Si_{12}O_{48} \cdot 27\ H_2O$ [zeolite A],

$Na_6Al_6Si_6O_{24} \cdot 2\ NaX \cdot 7.5\ H_2O$, X= OH, halogen, ClO_4 [sodalite]

$Na_6Al_6Si_{30}O_{72} \cdot 24\ H_2O$,

$Na_8Al_8Si_{40}O_{96} \cdot 24\ H_2O$,

$Na_{16}Al_{16}Si_{24}O_{80} \cdot 16\ H_2O$,

$Na_{16}Al_{16}Si_{32}O_{96} \cdot 16\ H_2O$,

$Na_{56}Al_{56}Si_{136}O_{384} \cdot 250\ H_2O$ [zeolite Y],

$Na_{86}Al_{86}Si_{106}O_{384} \cdot 264\ H_2O$ [zeolite X]

or those zeolites which can be described by partial or complete replacement of the sodium atoms with Li, K, Mg, Ca, Sr or Zn atoms, typically

$(Na,K)_{10}Al_{10}Si_{22}O_{64} \cdot 20\ H_2O$,

$Ca_{4.5}Na_3[(AlO_2)_{12}(SiO_2)_{12}] \cdot 30\ H_2O$,

$K_9Na_3[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27\ H_2O$.

The hydrotalcites and/or zeolites can be used in amounts of typically 0.1 to 20,

conveniently of 0.1 to 10 and, preferably, of 0.1 to 5 parts by weight, based on 100 parts by weight of [(c) +(d)].

Components (a) and (b) of the compositions as well as optional additives can also be added in the form of a masterbatch to the polymers to be stabilised. Said polymers can comprise typically 10 to 40 % by weight of component (a), 1 to 20 % by weight of component (b), as well as polymers of component (c) or (d), further stabilisers, such as processing assistants, lubricants, flame retardants, or a combination of these substances.

The compositions can be processed by injection moulding or extrusion to mouldings. The most important process for the preparation of mouldings from plastomers is the injection moulding process, which is well-known to the expert and described, inter alia, in Ullmanns Enzyklopädie der Technischen Chemie, Vol. 15, 304 ff. Extrusion is likewise such a standard process that the expert does not require any further details. The extrusion process is described, inter alia, in "Concise Encyclopedia of Polymer Science and Engineering", J.I. Kroschwitz ed., John Wiley & Sons, 1990, pp. 363-7. The extrusion process is used, for example, to prepare sheets, profiles and tubes.

The compositions are preferably used for the preparation of thermostable articles such as tubes, fittings and apparatus casings.

The following Examples illustrate the invention in more detail without, however, limiting it in any way. Here, as well as in the remainder of the description, parts and percentages are by weight, unless otherwise stated.

<u>Example 1:</u>

Because thermal and mechanical stresses of polymers are simulated, the described Brabender test serves as model system for the injection moulding and extrusion process. The test specimens obtained are models for mouldings.

46 g of the two PVC/ABS compounds described in Table I are subjected to thermal and fricative stress (by shear forces) in the kneading chamber of a Brabender plastograph at 45 rpm and 190°C. Samples (c. 0.5 g) are taken from the plastified PVC/ABS composition at intervals of 5 minutes and are then moulded to test specimens at 180°C over 1.5 min. The yellowness index of these samples is determined by colorimetric analysis (YI;

DIN 5033, ASTM 1925-70). Low yellowness indices signify good activity of the stabiliser.

In addition, the characterisation of the long-term thermostability is carried out on the basis of the time required until the torque increases through the crosslinking of the polymer material (Brabender degradation time). Accordingly, long degradation times signify good stabilisation. The results are set forth in the following Table I and show that stabilisation using the organotin compound and $NaClO_4$ is superior to that using only the organotin compounds.

Table I (amounts in parts by weight)

Brabender heat test at 190°C

Mixture	1	2
PVC (K value 50)	50	50
ABS	50	50
PMMA flow promoter[1)]	2.0	2.0
external lubricants[2)]	4.0	4.0
combination lubricant[3)]	0.8	0.8
TiO_2	3.0	3.0
chlorinated polyethylene	3.0	3.0
dibutyl tin maleate	0.5	0.5
dibutyl tin mercapto-propionate	1.5	1.5
$NaClO_4$	-	0.1

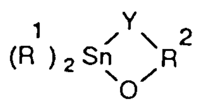
[1)]Polymethyl methacrylate PARALOID® K 125 [2)]high molecular weight multicomponent ester (LOXIOL® G70 S) [3)]LOXIOL® GS 1809

Brabender degradation time [minutes]	50	55
YI after 15 min.	18.0	17.6
YI after 20 min.	24.7	22.2
YI after 25 min.	35.5	29.3
YI after 30 min.	50.6	39.2
YI after 35 min.	63.4	50.8
YI after 40 min.	70.9	59.7
YI after 45 min.	78.0	64.7
YI after 50 min.	degrad.	67.5

What is claimed is

1. Use of

(a) at least one organotin compound of formula I or II



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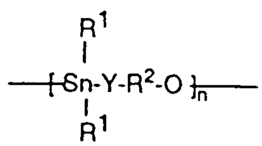
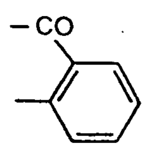


(II),

wherein n is a number from 1 to 6,

R^1 is C_4-C_8alkyl,

Y is -S- or -O- ,

if Y is -S-, then R^2 is -$(CH_2)_2$-CO- or  ,

if Y is -O- , then R^2 is -CO-R^3-CO- , and

R^3 is C_1-C_{12}alkylene, C_2-C_{12}alkenylene or o- or p-phenylene, as well as of

(b) at least one perchlorate of a mono- or divalent metal

for the preparation of a stabilised moulding having superior thermostability and consisting of a polymer composition, comprising

(c) 20-80 parts by weight of a vinyl chloride homopolymer (PVC),

(d) 80-20 parts by weight of at least one thermoplastic copolymer based on styrene and acrylonitrile

by an injection moulding or extrusion process.

2. Use according to claim 1, wherein

R^1 is butyl or octyl,

if Y is -S-,

then R^2 is $-(CH_2)_2$-CO- and,
if Y is -O-,
then R^2 is -CO-R^3-CO-, and
R^3 is -CH=CH- .

3. Use according to claim 1, wherein component (d) is 80-20 % by weight of at least one copolymer from the ABS and SAN group.

4. Use according to claim 1, wherein component (c) is 25-50 % by weight of PVC, and component (d) is 75-50 % by weight of at least one copolymer from the ABS and SAN group.

5. Use according to claim 1, wherein component (c) is 40-75 % by weight of PVC, and component (d) is 60-25 % by weight of at least one copolymer from the ABS and SAN group.

6. Use according to claim 1, wherein component (b) is at least one of the $NaClO_4$, $KClO_4$, $Ca(ClO_4)_2$ $Mg(ClO_4)_2$ or $Zn(ClO_4)_2$ substances.

7. Use according to claim 1, wherein lubricants, pigments, processing assistants, fillers, antioxidants and/or light stabilisers are additionally present.

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